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Exploring Athermal Initiation Mechanism of Azides

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October 1, 2009

14th International Detonation Symposium
Coeur d'Alene, ID, United States
April 11, 2010 through April 16, 2010

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Poster Presentation

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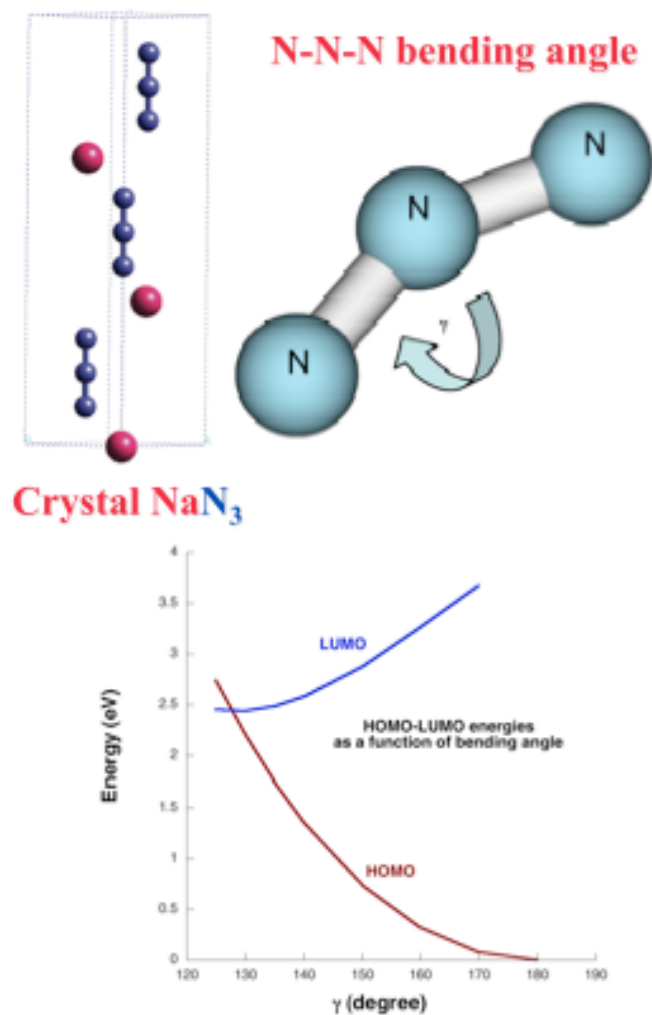
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ABSTRACT

In covalently bonded molecules, when bonds are stretched and bent, there are regions in the nuclear configuration space where the energies of the highest occupied molecular orbitals (HOMOs) and those of the lowest unoccupied molecular orbitals (LUMOs) become degenerate. HUMO-LUMO energy band closure due to bond-bending allows the electrons in the bonding states to expand at constant volume, eliminating the activation energy for decomposition and the occurrence of fast reactions. In periodic solids, the HOMO-LUMO gaps develop into band gaps; hence, a band gap closure and the delocalization of the valence band electrons (metallization) would be achieved via shear strains. Gilman has proposed that detonation fronts cause metallization via shear, and are thus, athermally activated.^{1, 2} Our recent ab initio calculations showed that in the case of TATB, the critical shear angle responsible for the vanishing of the energy band gap is achieved at near constant volume via a 55 degree bending of the nitro group out of the molecular plane.³ We explore the validity of an athermal mechanism via bending of the N-N-N bond in the azide ion N_3^- , which is omnipresent in metal azides such as sodium and lead azides. Density functional calculations showed that sodium azide (NaN_3) is an insulator with a band gap of 4.7 eV at ambient conditions. We calculate HUMO-LUMO energy gap as a function of bending of the N-N-N bond in N_3^- . We determined that, in accordance with Gilman's postulation, this bending causes the HOMO to rise in energy, while lowering that of the LUMO. The energy gap decreases until it completely vanishes at $\gamma=127^\circ$, indicating metallization. Several constant volume-temperature simulations of

NaN_3 also showed that the N-N-N bending motion increases as the temperature of the system increases, indicating that metallization can also be thermally activated at a threshold temperature.



References:

- 1- J. J. Gillman, *Bull. Am. Phys. Soc.* **37**, 361 (1992).
- 2- J. J. Gillman, *Phil. Mag. B* **67**, 207 (1993).
- 3- M. R. Manaa, *App. Phys. Lett.* **83**, 1352 (2003).

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.